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Inorganic chemistry: Cation o' nine tails**

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Abstract

The field of actinide chemistry is still young, not least because the radioactivity of these elements makes them difficult to work with. A study now reveals details of how actinide compounds might behave in water.

Main text

Reporting in *Angewandte Chemie*, Apostolidis *et al.*¹ describe how they combined synthesis, spectroscopy and computational modelling to identify, for the first time, a series of complexes in which water molecules bind to ions of the actinide elements — which include some of the heaviest and least-stable elements known.

Overcoming the difficulties associated with the intense radioactivity and complex chemistry of these metals, the authors found that one actinide cation binds directly to nine water molecules to form complex ions of the form $[\text{An}(\text{H}_2\text{O})_9]^{3+}$, where An is an actinide. Gaining such detailed knowledge of hydrated actinide cations is fundamental for understanding how the most radioactive components of nuclear waste behave in water. It will also allow chemists to optimize procedures to separate and extract actinides in the laboratory, as well as to understand and prevent actinide-ion migration in the environment.

The actinide series contains the elements thorium to lawrencium and is usually displayed as the bottom row of the periodic table (Fig. 1a). Together with the lanthanides (the row of elements directly above the actinides in the periodic table), the actinides form a family known as the *f*-block elements, named after their outermost,

incompletely filled electron orbitals, the *f* orbitals. The *f*-block elements are often insultingly referred to as the footnotes of the table, but it has to be admitted that the chemistry of the lanthanides in water, at least, is relatively straightforward. All lanthanide ions (generically abbreviated as Ln^{3+}) react with simple anions (X^- , typically the salts of strong acids), generating complexes of the form LnX_3 . And that's pretty much it. Compare this with the rich chemistry of the transition elements, which take part in redox reactions and form all sorts of different complexes.

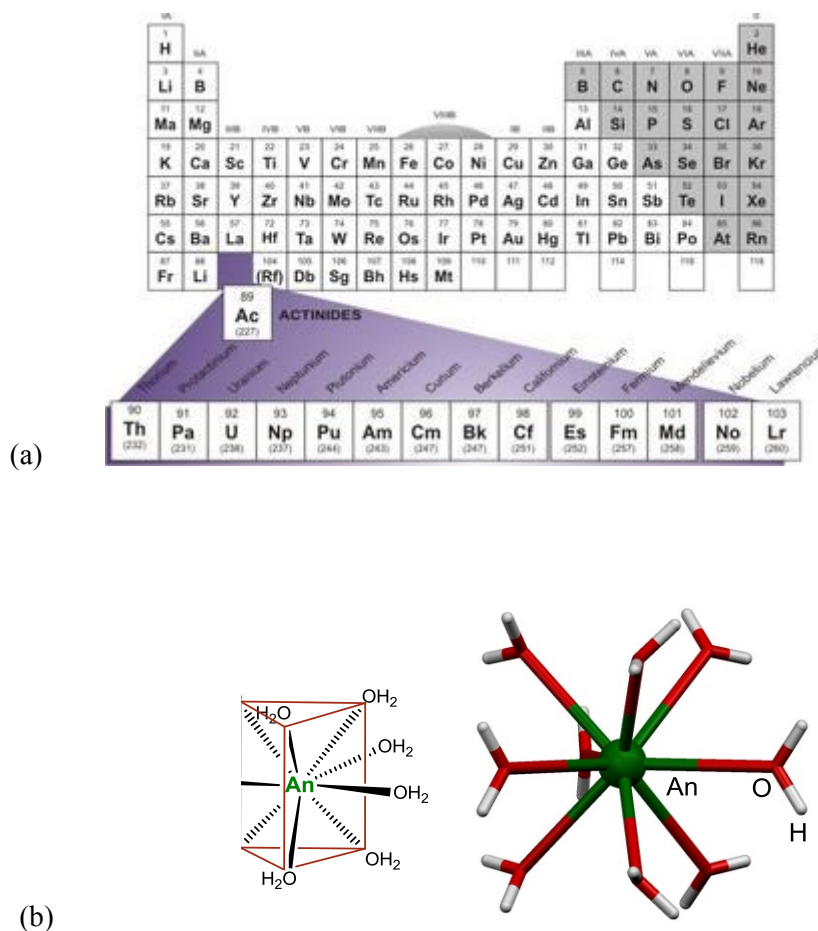


Figure 1. a) The actinides are the elements thorium to lawrencium. They follow on from actinium (Ac) in the periodic table, but are usually depicted as a separate row at the foot of the table. **b)** Apostolidis *et al.*¹ have characterized the cations — $[\text{An}(\text{H}_2\text{O})_9]^{3+}$, where An is an actinide — found in hydrated actinide triflate compounds. The structure shown here is for the californium compound, but all of the members of the series studied by the authors (uranium to curium, and californium) adopt the same symmetrical structure. The complete crystal structure includes triflate counterions, CF_3SO_3^- , but these have been omitted here for clarity. The actinide cation is depicted in green; the red and grey spheres represent the oxygen and hydrogen atoms, respectively, of the nine bound water molecules.

So why is lanthanide chemistry so much less diverse than transition-metal chemistry? The answer is electronic — the number of valence (outermost) electrons that can be removed from transition-metal atoms varies, whereas in general only three valence electrons are removable from *f*-block atoms. The remaining valence electrons sit in multi-lobed orbitals (shaped like flower petals) that do not extend far enough from the atom to overlap the orbitals of the atoms in the ligand, and so do not participate in bonding. To use our flower analogy, the lobes of *f* orbitals are tiny daisy petals compared with the giant poppy petals of transition-metal valence orbitals. Nevertheless, the 'hidden'*f*-orbital electrons of lanthanides give their ions interesting spectroscopic and magnetic properties.

But what of the actinides, the lanthanides' radioactive siblings in the *f*-block family of elements? The actinides have unique properties and, in an increasingly nuclear age, it is crucial to understand their behaviour — especially in water, if we are to gauge the risks of actinide-containing nuclear waste in the environment. In this respect, 'triflate' salts of actinides ($\text{An}^{3+}(\text{CF}_3\text{SO}_3^-)_3$, where CF_3SO_3^- is a triflate anion) are useful model compounds. Triflate anions can bind directly to *f*-block cations, but they are readily displaced by other ligand molecules, such as water, that bind more strongly. For lanthanides, the resultant complexes are known to consist of a central *f*-block cation surrounded by nine water molecules (known as the primary coordination sphere), to which the triflate ions bind in turn (forming the secondary coordination sphere). These water-stable, water-soluble lanthanide triflates have been used for 20 years as catalysts for a range of organic transformations². But making and studying the analogous actinide triflates presents a series of challenges.

Apostolidis *et al.*¹ have overcome these challenges in their syntheses of hydrated triflates for the block of actinides from uranium to curium, as well as for californium. The lighter, naturally occurring, actinides (those up to uranium in the periodic table) are only mildly radioactive, which simplifies handling. The main practical problem associated with these elements is that they can take part in unwanted oxidation reactions, and so the authors had to use careful synthetic techniques to avoid oxidation when they made uranium triflate. Similar techniques were also required when the authors made the triflates of the heavier elements neptunium and plutonium.

After uranium on the periodic table are the 'transuranic' metals, which are man-made. These elements are at least 100,000-fold more radioactive than uranium, and their half-lives are markedly shorter. Pure samples of transuranic salts and complexes quickly undergo radioactive decay to produce daughter products, and the energy released in the process damages any bound ligands. The authors therefore needed to rapidly synthesize and identify the triflates made from transuranic starting materials, before the samples became too contaminated with decay products. When making californium triflate, Apostolidis *et al.* chose an isotope of the element (^{249}Cf) with a long enough half-life that they did not have to rush the synthesis. In this case, the main practical challenge was californium's high level of radioactivity, a problem that the authors overcame by working at the microgram scale.

Perhaps surprisingly, Apostolidis *et al.* found that the same highly symmetrical cation, in which nine water molecules make up the primary coordination sphere, is formed for all of the actinides studied, despite the changes in cation size that occur throughout the series (Fig. 1b). What's more, this behaviour mirrors that of the lanthanide ions — a similarity that was not necessarily a given. These findings will help to guide predictions of the further reactions of the actinides.

Triflate anions in the secondary coordination sphere of the actinide complexes¹ help to hold the water molecules in fixed positions through a large number of weak hydrogen-bonding interactions, in the same way that water molecules in ice crystals are held together by a symmetrical network of hydrogen bonds. The networks of bonds within the complexes will also have allowed the growth of the high-quality single crystals used by the authors in their X-ray studies. Single-crystal X-ray studies on transuranic compounds are rare, because the crystals are so 'hot' that they tend to self-destruct during analysis, owing to internal irradiation. Californium triflate is therefore one of just a handful of transuranic compounds^{3,4} to be analysed by this method. Of the previously published compounds, one⁴ has the same nine-fold geometry as Apostolidis and colleagues' triflates¹.

The *f*-orbital electrons in the triflate complexes undergo transitions that allow detailed spectroscopic and magnetic analysis. This provides fundamental information about the ordering of the *f*-electron energy levels in the complexes and shows that the early actinide triflates are strongly ionic, and behave remarkably like lanthanides in water. The electronic transitions also give the compounds their beautiful colours, ranging from smoky blues and olive greens to vibrant pinks.

The stunning colours are not, in themselves, enough to encourage more synthetic chemists to study actinide cations. But other factors are certainly promoting a renaissance in uranium chemistry^{5,6,7} — including the ready availability of uranium triiodide, which can be used as a precursor to uranium complexes. Replacing triflate anions in lanthanide complexes with anionic groups that bind more strongly to the cation has also been effective for synthesizing new complexes and catalysts^{8,9,10}. Exciting new actinide chemistry is therefore sure to follow from studies such as those of Apostolidis and colleagues.

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